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(54) **Infrared phosphor and material having latent images and optical reading system using said phosphor**

Infrarot-Phosphor und Material mit latenten Bildern und optisches Auslesesystem brauchend dieses Phosphor

Matériau luminescent infrarouge et matériau à images latentes et système de lecture optique utilisant ce matériau luminescent

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DE-A- 2 750 321 **FR-A- 2 382 490**
GB-A- 2 013 233 **US-A- 4 149 989**
US-A- 4 202 491

EP 0 624 636 B1

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Description

[0001] The present invention relates to an infrared phosphor which is excited by irradiation with infrared rays to emit light of infrared wavelength region, and to a material having latent images and an optical reading system which use said infrared phosphor.

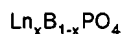
[0002] Recently, in various industries such as the distribution industry, control of goods by means of bar codes is extensively conducted and furthermore, bar codes are printed on various prepaid cards and passing cards and these bar codes are read by optical reading apparatuses such as scanners to perform the desired actions. Moreover, various attempts have been made to apply forgery preventive means to credit cards and prepaid cards or to detect forged cards. According to one of them, the marks such as bar codes are printed with an ink containing a phosphor by offset printing or by using an ink ribbon to form latent image marks, the latent image marks are irradiated with a semiconductor laser beam to excite the phosphor and the light emitted from the phosphor is received to read the bar code information by an optical reading apparatus.

[0003] The phosphors used in the above-mentioned method are those which are described in USP 4,202,491.

[0004] However, the conventional phosphors have a large particle size of larger than 5 μm and cannot be used as they are in the inks used for offset printing or ink ribbons and they must be ground. During this grinding step, crystallinity and composition of the phosphors are damaged to cause considerable reduction in luminous intensity. Another problem is reduction in productivity due to the increase in the number of steps. For this reason, the systems in which the above phosphors are used have not yet been able to be put to practical use.

[0005] Accordingly, the object of the present invention is to solve the problem of the particle size encountered with the aforementioned conventional products, namely, to synthesize infrared phosphors of fine particles suitable to be used in inks for offset printing or ink ribbons without the step of grinding and to provide materials having latent images and optical reading systems which use the thus obtained infrared phosphors.

[0006] The first invention for attaining the above object is an infrared phosphor comprising a phosphate represented by the following formula:



wherein B represents at least one of Y, La, Gd, Bi, Ce, Lu, In, Pr and Tb; Ln represents at least one of Nd, Yb and Er; and x is from 0.01 to 0.99.

[0007] An Example is YPO_4Yb . The infrared phosphor can be excited by infrared rays to emit infrared rays and has a nonacicular particle shape and a particle size of 4 μm or smaller after synthesis.

[0008] The second invention for attaining the above object is a material having a latent image which comprises a substrate and provided thereon a print layer comprising (a) a phosphor excitable by infrared rays and having a nonacicular particle shape and a particle size of 4 μm or smaller, and (b) an infrared transmitting binder such as wax or vinyl chloride-vinyl acetate copolymer, the infrared phosphor comprising a phosphate as defined above.

[0009] The third invention for attaining the above object is an optical reading system according to which an infrared phosphor (comprising a phosphate as defined above) having a nonacicular particle shape and a particle size of 4 μm or smaller is used, and said infrared phosphor is excitable with infrared rays emitted from a light emitting device having a wavelength of luminescence centre of 700-1,000 nm, and afterglow emitted from the infrared phosphor when the light emitting device is turned off is detectable by a photo detector which can receive light having a wavelength from 800-1,600 nm.

[0010] The infrared phosphor used in the present invention which comprises an oxyacid salt-containing compound, namely the phosphate defined above, and which has a nonacicular particle shape and has a particle size of 4 μm or smaller, has a much smaller particle size than conventional infrared phosphors and can be applied to materials having latent images formed by offset printing or using ink ribbons and to optical reading systems. Thus, the present invention provides conspicuous effects for practical use of systems which use infrared phosphors.

[0011] Fig.1 is a sectional view of a bar code reader provided with the optical reading apparatus of an example according to the present invention.

[0012] Fig. 2 is an oblique view of essential parts of a dismounted reading head in the optical reading apparatus of an example according to the present invention.

[0013] Fig.3 is a sectional view of the reading head in the direction of X-X of Fig.2.

[0014] Fig. 4 is a sectional view of the reading head in the direction of Y-Y of Fig. 2.

[0015] Fig. 5 is a plan view of the card used in the example according to the present invention.

[0016] Fig.6 is an enlarged sectional view of essential parts of the card.

[0017] Fig. 7 is a characteristic curve which shows the relation between thickness of the print layer of the card and output voltage.

[0018] Figs. 8A, 8B, 8C and 8D show timing charts of the light emitting device and the photo detector in the optical reading apparatus in the example according to the present invention.

[0019] Figs. 9A, 9B and 9C show scanning electron microphotographs of the particles in Example 1, Comparative Example 1 and Example 10, respectively.

5 **[0020]** Figs. 10A and 10B are an emission spectrum of the phosphor in Example 1 and Comparative Example 1, respectively.

[0021] Fig. 11 is an emission spectrum of the phosphor in Example 12.

[0022] In the drawings, the main reference numerals indicate the following:

- 10 1 Body of apparatus
- 2 Reading head
- 4 Card
- 9 Light emitting device
- 10 Photo detector
- 15 12 Bar code pattern
- 27 Card substrate
- 28 Bar code pattern
- 29 Print layer

20 **[0023]** An example of the present invention will be explained referring to the drawings.

[0024] As shown in Fig. 1, the optical reading apparatus (bar code reader) is mainly composed of body 1, reading head 2 mounted in the body 1 and printed circuit board 3 which is connected to the reading head 2 and on which devices conducting various controls as mentioned hereinafter are mounted.

25 **[0025]** As shown in Fig. 1, a guide groove 5 through which the card 4 is allowed to pass is provided in the upper part of the body 1 and the reading head 2 is provided to face the card from the inner wall surface of the guide groove 5.

[0026] The card 4 bearing the bar code pattern described hereinafter is passed by hand through the guide groove 5 in the direction of the arrow, during which the information of the bar code pattern is optically read by the reading head 2.

30 **[0027]** As shown in Fig. 2, the reading head 2 comprises head body 6 which also serves as a case, slit sheet 7 inserted into the head body 6, sheet pressing member 8 which also serves as a holder for devices, light emitting device 9 and photo detector 10 held by the sheet pressing member 8, and head cover 11 which covers the upper opening of the head body 6.

[0028] At the center of the underside of the head body 6 is formed an opening 13 in parallel to the longitudinal direction of the bar code pattern 28 (see Fig. 5) formed on the card 4, and as shown in Fig. 3, engaging stepped portion 14 is provided on both sides of the underside of the head body.

35 **[0029]** Inside the head body 6, there are formed sheet-receiving faces 15, 15 inclined from both sides towards the opening 13, and pins 16 are provided midway the sheet-receiving faces 15, 15 projecting from the sheet-receiving face (see Fig. 2) and detent grooves 17 are provided at both end portions of the opening 13 (see Fig. 2).

[0030] As shown in Fig. 2 and Fig. 3, flange portions 18, 18 for fitting the reading head 2 to the body 1 are provided in the vicinity of the upper opening of head body 6 projecting from the head body.

40 **[0031]** As shown in Fig. 2, the slit sheet 7 is a flexible sheet comprising a base film of a transparent synthetic resin film such as polyethylene terephthalate (PET) film and a black print layer 20 formed on the base film excluding the slit-like light transmitting portion 19. Holes 21 are provided in the front and rear parts of the slit sheet 7 and the position of the slit sheet 7 on the head body 6 is determined by inserting the pins 16 of the head body 6 into the holes 21, respectively and the slit-like light transmitting portion 19 of the slit sheet 7 is positioned at the center of the opening 13

45 of the head body 6 as shown in Fig. 3.
[0032] In this example, the slit sheet 7 used comprises a transparent base film on which the print layer 20 is formed, but there may also be used a slit sheet of a metallic thin sheet such as of stainless steel in which a slit-like groove is formed.

50 **[0033]** As shown in Fig. 2 and Fig. 3, the underside of the sheet pressing member 8 is curved in conformity with the sheet receiving face 15 of the head body 6 and the slit sheet 7 is mechanically interposed between the underside of the sheet pressing member 8 and the sheet receiving face 15 of the head body 6 and the light transmitting portion 19 of the slit sheet 7 is pushed out into the opening 13 of the head body 6. A slit-like light controlling hole 22 is formed at the center of the sheet pressing member 8 and faces the light transmitting portion 19 as shown in Fig. 3.

55 **[0034]** Detent pieces 23, 23 having a T-type planar shape are provided integrally projecting from both sides of the sheet pressing member 8 (see Fig. 2) and the sheet pressing member 8 is mounted in the head body 6 by fixing the detent pieces 23, 23 into the detent grooves 17, 17 of the head body 6.

[0035] Holding wall 24 in the form of a partial circular arc is provided extending upwardly on the sheet pressing member 8, and as shown in Fig. 4, the top portions of the light emitting device 9 and the photo detector 10 are inserted

in the holding wall 24 and held therein.

[0036] As the light transmitting device 9, there may be used one which emits infrared rays including near infrared rays and has a center wavelength of 700-960 nm and a light transmitting diode of 810 nm and 940 nm in center wavelength is used in the example.

5 [0037] As the photo detector 10, there may be used photo detectors made of Ge, In-Ga-As, PbS, PbSe or the like which can detect the light in the range of 800-1,600 nm which is in the region of the emitted light wavelength.

[0038] Four engaging claws 25 are provided at the peripheral portion of the head cover 11 projecting therefrom downwardly, and as shown in Fig. 3, these engaging claws 25 are engaged with the engaging stepped portions 14 of the head body 6 and thus, fabrication of the reading head 2 is completed.

10 [0039] On the inner surface of the head cover 11 are provided leg portions 26 projecting downwardly as shown in Fig. 3. When mounting of head cover 11 is completed as shown in Fig. 3, the sheet pressing member 8 is pressed towards the sheet receiving face 15 by the leg portions 26 through the light emitting device 9 and photo detector 10 and the slit sheet 7 is surely fixed.

[0040] The construction of card 4 will be explained referring to Fig. 5 and Fig. 6. The card 4 is used, for example, as various prepaid cards, telephone cards, passage cards.

[0041] Fig. 5 is a plan view of the card and Fig. 6 is an enlarged sectional view of essential parts of the card.

[0042] As shown in Fig. 5, print layer 29 having bar code pattern 28 of latent image is formed on the surface of card substrate 27. The card substrate 27 comprises, for example, a polyvinyl chloride sheet in which a white pigment such as titanium oxide is dispersed and retained and has the property to reflect infrared rays.

20 [0043] On the print layer 29 is printed a desired bar code pattern 28 with an ink comprising a phosphor which can be excited by irradiation with infrared rays and a transparent (infrared transmitting) binder in which the phosphor is dispersed and retained.

[0044] The phosphor comprises an oxyacid salt-containing compound containing at least one of Nd, Yb and Er.

25 [0045] Phosphate compounds are used because they are superior in chemical resistance to vanadate, borate, molybdate and tungstate alternatives.

[0046] Compositional ratio of the charged starting materials, firing temperature, and composition and particle size of the resulting infrared phosphors in specific preparation examples of the infrared phosphors are shown the Table below.

30 [0047] All of the samples of the Table were prepared by firing the starting materials at the respective temperatures for 2 hours, treating the fired products with hot water, further treating them with nitric acid (1 mol), and then washing the products with water.

[0048] Scanning electron microphotographs of the infrared phosphors obtained in Examples 1 and 10 and Comparative Example 1 are shown in Fig. 10 and emission spectra thereof are shown in Figs. 11 and 12.

35 [0049] The content of phosphor fine particles is suitably 50-80% by weight and this is 75% by weight in this example. When the content is less than 50% by weight, output from the print layer 29 is small and when it is more than 80% by weight, printability of the print layer 29 (bar code pattern) deteriorates, which may cause failure in printing.

[0050] The binders include, for example, wax, vinyl chloride-vinyl acetate copolymer, ethylene-vinyl acetate copolymer, polyester, polyurethane, and polycarbonate. These are used each alone or in admixture of two or more. If necessary, plasticizer, surface active agent and others may further be added.

40 [0051] The phosphor fine particles emit light upon being excited by infrared rays and in order to perform effective excitation of the phosphor fine particles, reflectance of the substrate 27 is set at 20% or higher. That is, by allowing the substrate to have a high reflectance, the infrared rays are reflected at the surface of the substrate 27 to accelerate the excitation of the phosphor fine particles. The reflectance of the substrate 27 can be enhanced by dispersing a white pigment such as titanium oxide in the substrate 27 and retaining it therein as aforementioned. The substrate 27 having a reflectance of 80% is used in this example.

45 [0052] The following table shows the results of measurement of output voltage and S/N of the print layer 29 when the light reflectance of the substrate 29 is variously changed by adjusting the content of the white pigment.

Table

Reflectance of substrate (%)	Output voltage (mV)	S/N
2	23	1.10
5	36	1.25
20	61	1.61
30	77	1.83
50	120	2.51
60	130	2.93

Table (continued)

Reflectance of substrate (%)	Output voltage (mV)	S/N
80	580	3.60

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[0053] As is clear from the above table, when the reflectance of the substrate 27 is lower than 20%, sufficient output voltage cannot be obtained and furthermore, S/N is small and therefore, the information cannot be accurately read. On the other hand, when the reflectance of the substrate 27 is 20% or higher, preferably 50% or higher, the output voltage and the S/N are high and the information can be accurately read.

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[0054] Fig. 7 is a characteristic curve which shows the relation between the thickness of the print layer 29 and the output voltage. The abscissa axis shows the thickness of the print layer 29 and the ordinate axis shows the output voltage generated by excitation of the print layer 29.

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[0055] In Fig. 7, A is a characteristic curve which shows the relation between the thickness and the output voltage of the print layer 29 when the print layer 29 is formed on substrate 27 containing a white pigment as aforementioned. The straight line B is a line which shows an output level where the output of the print layer 29 reaches 1.6 time the output voltage of only the substrate containing the pigment (average reflectance to the visible light: 80%).

20

[0056] Results of various experiments conducted by the inventors show that when the output voltage of print layer 29 is lower than the level of the straight line B, the information of print layer 29 cannot be sufficiently read and therefore, the output voltage of print layer 29 is required to be higher than 1.6 time this output voltage (straight line B) and the minimum thickness of the print layer 29 at that time is 0.5 μm as is clear from Fig. 8. With increase in the thickness of print layer 29, the output voltage increases, but becomes nearly constant when the thickness is 50 μm .

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[0057] When the thickness of print layer 29 exceeds 50 μm , the presence of the print layer 29 of latent image is perceived depending on the condition of reflection of light. Therefore, it is preferred to limit the thickness of print layer 29 to the range of 0.5-50 μm .

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[0058] The presence of the print layer 29 can be concealed by forming a hiding layer (not shown) on the whole surface of the card substrate 27 having the print layer 29 thereon so as to cover the print layer 29 (bar code pattern 28).

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[0059] The print layer 29 and the hiding layer can be formed by, for example, heat transfer, ink jet, offset printing, and screen printing. Of these methods, the method of successively forming the print layer 29 and the hiding layer by heat transfer using an ink ribbon is especially preferred since the print layer containing the phosphor fine particles in a high concentration can be formed and furthermore, layers of the desired thickness can be surely obtained.

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[0060] Fig. 8 shows timing charts which illustrate the timing of light emission from the light emitting device 9 and the output state of the photo detector 10.

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[0061] As shown in Fig. 8A, the light emitting device 9 works on and off at a nearly equal interval of 500 μsec in its light-on time T_1 and light-off time T_2 and intermittently irradiates the print layer 29 with infrared rays. In Fig. 8, S_1 indicates the light-on signal of light emitting device 9.

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[0062] The charts in Figs. 8B, and 8C show the output state of the photo detector 10 when it detects the bar code pattern 28 (print layer 29) and the phosphor fine particles in the bar code pattern are excited by the infrared rays emitted from the light emitting device 9. Therefore, the output increases until the light-on of the light emitting device 9 has ceased as shown in Fig. 8B. Even when irradiation from the light emitting device 9 is stopped, the photo detector 10 detects the afterglow emitted from the bar code pattern 28. Since this afterglow decreases with lapse of timer if a standard value V_s is previously set, a square signal S_3 is obtained just after lighting-off of the light emitting device 9 by comparing the detected afterglow with the standard value V_s .

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[0063] Accordingly, the bar code information of the bar code pattern 28 can be optically read by repeating the lighting-on and the lighting-off of the light emitting device 9 with every minute period of time.

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[0064] As mentioned above, in the method of detecting the afterglow of phosphors, since the light emitting device is off in optical reading of the phosphor, there is no reflected light and so the fluorescence can be detected without using expensive optical filters. Thus, small and inexpensive optical reading systems can be provided.

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[0065] Fig. 8C shows a method of detecting the afterglow from the phosphor, but the light emitted from the phosphor when the light emitting device is on can be detected by using a filter which intercepts the light in the wavelength region of luminescence center of the light emitting device and transmits the light in the wavelength region of the luminescence center of phosphors. Fig. 8D shows the output state of photo detector 10 in that case.

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[0066] In the above example, reading of bar code has been explained.

[0067] Other marks such as figures, symbols and marks of peculiar shapes can also be read.

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[0068] In the above example, explanation has been given on using card, but information of recording media in the other forms such as sheet, bag, and slip can also be read.

[0069] The optical reading system of the present invention has the following uses and characteristics.

1. For factory automation (FA):

Control in fabrication of automobiles and others. That is, types, countries to which they are to be exported, dates of manufacture, lots of manufacture and others can be controlled using latent image marks without damaging the appearance.

2. In the case of the conventional reflection type bar codes, those which are marked on black materials such as tires or on transparent materials such as glass and plastics cannot be read while these can be read in the case of the latent image marks.

3. Even if letters or designs are printed on the latent image marks, the latent image marks can be read. Therefore, small spaces such as price tags and goods tags can be effectively utilized.

4. For the same reasons as of the above 1 and 3, the system is effective for goods whose design is regarded as important such as cosmetics and drugs or various fancy boxes and packages required to have a feeling of high quality.

5. Under such environments as factories or working fields, the conventional reflective type bar codes cannot be used because of contamination by oil or dust while the latent image marks can be read even under these conditions.

6. For the same reasons as of the above 1 and 3, management information of manufacturers can be put in delivery slips for customers as concealed codes (normally, delivery slips can contain only the information necessary for customers with a blank and format approved by the customers).

7. A card in which an information is put as a concealed code can be used as a game card (bar code game).

8. For the same reasons as of the above 1 and 3, the system can be used for care of books, publications and drawings without damaging the designs.

9. According to the present system, forgery, alteration and falsification are difficult and the system can be applied to control of getting in and out of a room or attending and leaving the office, and to key cards of hotels.

10. Forgery, alteration and falsification of securities or stocks can be prevented.

11. Forgery, alteration and falsification of, for example credit cards, cash cards and telephone cards can be prevented.

12. Forgery, alteration and falsification of, for example student's identification card and ID cards can be prevented and besides, can be reduced in size and can be saved in their space.

13. Forgery, alteration and falsification of, for example stamp cards and point cards can be prevented and besides, can be reduced in their size and can be saved in their space.

14. Forgery, alteration and falsification of, for example pari-mutuel tickets and bicycle-race tickets can be prevented.

15. Forgery, alteration and falsification can be prevented by introducing into prize exchanging systems of pinball.

Table

	Charged starting materials (g)										
	Nd ₂ O ₃	Yb ₂ O ₃	Er ₂ O ₃	Gd ₂ O ₃	Y ₂ O ₃	La ₂ O ₃	-	-	Li ₂ O ₃	NH ₄ H ₂ PO ₄	LiH ₂ PO ₄
Example 1	3.5	4.0	-	-	17.5	-				-	65.0
" 2	3.5	4.0	-	3.6	15.3	-				-	65.0
" 3	3.5	4.0	-	3.6	15.3	-				10.0	31.0
" 4	0.8	-	-	-	21.5	-				-	65.0
" 5	0.8	-	-	-	15.3	9.8				-	65.0
" 6	0.8	-	-	24.5	-	9.8					65.0
" 7	-	2.5	-	-	12.7	-				-	65.0
" 8	-	2.5	-	16.8	-	-				-	65.0
" 9	-	7.4	0.1	-	9.8	-					65.0
" 10	-	-	0.1	-	6.7	-				-	65.0
-											
-											
Comparative Example 1	30.0	4.0	-	-	-	-	-	-	11.0	14.0	-

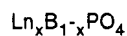
- Cont'd -

Table (Cont'd)

Firing temperature (°C)	Composition of infrared phosphor	Particle size (μm)
700	Nd _{0.1} Yb _{0.1} Y _{0.8} PO ₄	0.6
750	Nd _{0.1} Yb _{0.1} Gd _{0.1} Y _{0.7} PO ₄	0.8
670	Nd _{0.1} Yb _{0.1} Gd _{0.1} Y _{0.7} PO ₄	0.4
850	Nd _{0.02} Y _{0.98} PO ₄	2.6
750	Nd _{0.02} La _{0.3} Y _{0.68} PO ₄	1.0
700	Nd _{0.02} La _{0.3} Gd _{0.68} PO ₄	3.3
750	Yb _{0.1} Y _{0.9} PO ₄	1.0
850	Yb _{0.1} Gd _{0.9} PO ₄	3.5
750	Yb _{0.3} Er _{0.005} Y _{0.695} PO ₄	0.9
750	Er _{0.005} Y _{0.995} PO ₄	0.9
750	LiNd _{0.9} Yb _{0.1} P ₄ O ₁₂	6.0

Claims

1. An infrared phosphor excitable by infrared rays to emit infrared rays which has a nonacicular particle shape and a particle size of 4 μm or smaller after synthesis comprising a phosphate compound represented by the following formula:

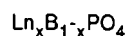


wherein B represents at least one of Y, La, Gd, Bi, Ce, Lu, In, Pr and Tb; Ln represents at least one of Nd, Yb and Er; and x is from 0.01 to 0.99.

2. An infrared phosphor according to claim 1, wherein the wavelength of the exciting light coincides with that of the emitted light at room temperature.
3. A material having a latent image which comprises a substrate and provided thereon a print layer comprising (a) a

print layer comprising (a) a phosphor excitable by infrared rays and having a nonacicular particle shape and a particle size of 4 µm or smaller, and (b) an infrared transmitting binder, the phosphor comprising a phosphate compound represented by the following formula:

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wherein B represents at least one of Y, La, Gd, Bi, Ce, Lu, In, Pr and Tb; Ln represents at least one of Nd, Yb and Er; x is from 0.01 to 0.99.

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4. A material according to claim 3, wherein the wavelength of the exciting light coincides with that of the emitted light at room temperature.

5. A material according to claim 3, wherein thickness of the print layer is in the range of 0.5 to 50 µm.

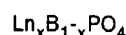
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6. A material according to claim 3, wherein light reflectance of the surface of the substrate on which the print layer is provided is 20% or higher.

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7. An optical reading system according to which an infrared phosphor having a nonacicular particle shape and a particle size of 4 µm or smaller is used, and said infrared phosphor is excitable with infrared rays emitted from a light emitting device having a wavelength of luminescence centre of 700-1,000 nm, and afterglow emitted from the infrared phosphor when the light emitting device is off is detectable by a photo detector which can receive light having a wavelength from 800 to 1,600 nm, the phosphor comprising a phosphate compound represented by the following formula:

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wherein B represents at least one of Y, La, Gd, Bi, Ce, Lu, In, Pr and Tb; Ln represents at least one of Nd, Yb and Er; and x is from 0.01 to 0.99.

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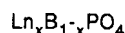
8. An optical reading system according to claim 7 wherein the wavelength of the exciting light coincides with that of the emitted light at room temperature.

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Patentansprüche

1. Infrarot-Phosphor, der durch Infrarotstrahlen dazu anregbar ist, Infrarotstrahlen zu emittieren, welcher eine nicht-azikuläre Teilchenform und eine Teilchengröße von 4 µm oder weniger nach der Synthese aufweist, der eine Phosphat-Verbindung der folgenden allgemeinen Formel:

40



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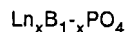
umfasst, in der B mindestens eines der Elemente Y, La, Gd, Bi, Ce, Lu, In, Pr und Tb darstellt, Ln mindestens eines der Elemente Nd, Yb und Er darstellt und x 0,01 - 0,99 beträgt.

2. Infrarot-Phosphor nach Anspruch 1, wobei die Wellenlänge des Anregungslichtes mit der des bei Raumtemperatur emittierten Lichtes koinzident ist.

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3. Material mit einem latenten Bild, welches ein Substrat und eine darauf vorgesehene Druckschicht aufweist, die (a) eine Druckschicht aufweist, welche (a) einen Phosphor, der durch Infrarotstrahlen anregbar ist und eine nicht-azikuläre Teilchenform und eine Teilchengröße von 4 µm oder weniger aufweist, und (b) einen infrarot-übertragenden Binder aufweist, wobei der Phosphor eine Phosphat-Verbindung mit der folgenden allgemeinen Formel:

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umfasst, in der B mindestens eines der Elemente Y, La, Gd, Bi, Ce, Lu, In, Pr und Tb darstellt, Ln mindestens eines der Elemente Nd, Yb und Er darstellt und x 0,01 - 0,99 beträgt.

- 5 4. Material nach Anspruch 3, wobei die Wellenlänge des Anregungslichtes mit der des bei Raumtemperatur emittierten Lichtes koinzident ist.
5. Material nach Anspruch 3, wobei die Dicke der Druckschicht im Bereich von 0,5 - 50 µm liegt.
- 10 6. Material nach Anspruch 3, wobei die Lichtreflektion der Oberfläche des Substrates, auf dem die Druckschicht vorgesehen ist, 20% oder mehr beträgt.
- 15 7. Optisches Lesesystem, in dem ein Infrarot-Phosphor mit einer nicht-azikulären Teilchenform und einer Teilchengröße von 4 µm oder weniger verwendet wird, wobei der Infrarot-Phosphor mit Infrarotstrahlen anregbar ist, die von einer Licht emittierenden Vorrichtung mit einer Wellenlänge im Lumineszenzzentrum von 700 - 1000 nm emittiert werden, und das Nachleuchten, dass von dem Infrarot-Phosphor emittiert wird, wenn die Licht emittierende Vorrichtung ausgeschaltet ist, mit einem Photodetektor nachweisbar ist, der Licht mit einer Wellenlänge von 800 - 1600 nm empfangen kann, wobei der Phosphor eine Phosphat-Verbindung mit der folgenden Formel:



umfasst, in der B mindestens eines der Elemente Y, La, Gd, Bi, Ce, Lu, In, Pr und Tb darstellt, Ln mindestens eines der Elemente Nd, Yb und Er darstellt und x 0,01 - 0,99 beträgt.

- 25 8. Optisches Lesesystem nach Anspruch 7, wobei die Wellenlänge des Anregungslichtes mit der des bei Raumtemperatur emittierten Lichtes koinzident ist.

Revendications

- 30 1. Matière luminescente à infrarouge pouvant être excitée par les rayons infrarouges, qui a une forme de particule non aciculaire et une taille de particule de 4 µm ou moins après synthèse, comprenant un phosphate représenté par la formule :



où B représente au moins un élément parmi Y, La, Gd, Bi, Ce, Lu, In, Pr et Tb, Ln représente au moins un élément parmi Nd, Yb et Er, et x est compris dans l'intervalle allant de 0,01 à 0,99.

- 40 2. Matière luminescente à infrarouge selon la revendication 1, dans laquelle la longueur d'onde de la lumière d'excitation coïncide avec celle de la lumière émise à la température ambiante.
- 45 3. Matériau comportant une image latente qui comprend un substrat et muni d'une couche d'impression comprenant (a) une couche d'impression comprenant (a) une matière luminescente pouvant être excitée par des rayons infrarouges et ayant une forme de particule non aciculaire et une taille de particule de 4 µm ou moins, et (b) un liant transmettant le rayonnement infrarouge, la matière luminescente comprenant un phosphate représenté par la formule :



où B représente au moins un élément parmi Y, La, Gd, Bi, Ce, Lu, In, Pr et Tb, Ln représente au moins un élément parmi Nd, Yb et Er, et x est compris dans l'intervalle allant de 0,01 à 0,99.

- 55 4. Matériau selon la revendication 3, dans lequel la longueur d'onde de la lumière d'excitation coïncide avec celle de la lumière émise à la température ambiante.

5. Matériau selon la revendication 3, dans lequel l'épaisseur de la couche d'impression est comprise dans la page allant de 0,5 à 50 µm.
- 5 6. Matériau selon la revendication 3, dans lequel la réflexion lumineuse de la surface du substrat sur lequel est prévue la couche d'impression est supérieure ou égale à 20 %.
7. Système de lecture optique dans lequel est utilisée une matière luminescente à infrarouge ayant une forme de particule non aciculaire et une taille de particule de 4 µm ou moins, et ladite matière uminescente à infrarouge peut être excitée par des rayons infrarouges émis par un dispositif d'émission de lumière ayant une longueur d'onde de centre de luminescence de 700 à 1 000 nm, et la rémanence émise par la matière luminescente à infrarouge quand le dispositif d'émission de lumière est éteint est détectable par un photodétecteur qui peut recevoir de la lumière ayant une longueur d'onde comprise entre 800 et 1 600 nm, la matière luminescente comprenant un phosphate représenté par la formule
10
15
$$\text{Ln}_x\text{B}_{1-x}\text{PO}_4$$

où B représente au moins un élément parmi Y, La, Gd, Bi, Ce, Lu, In, Pr et Tb, Ln représente au moins un élément parmi Nd, Yb et Er, et x est compris dans l'intervalle allant de 0,01 à 0,99.

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8. Système de lecture optique selon la revendication 7 dans lequel la longueur, d'onde de la lumière d'excitation coïncide avec celle de la lumière émise à la température ambiante.

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FIG. 1

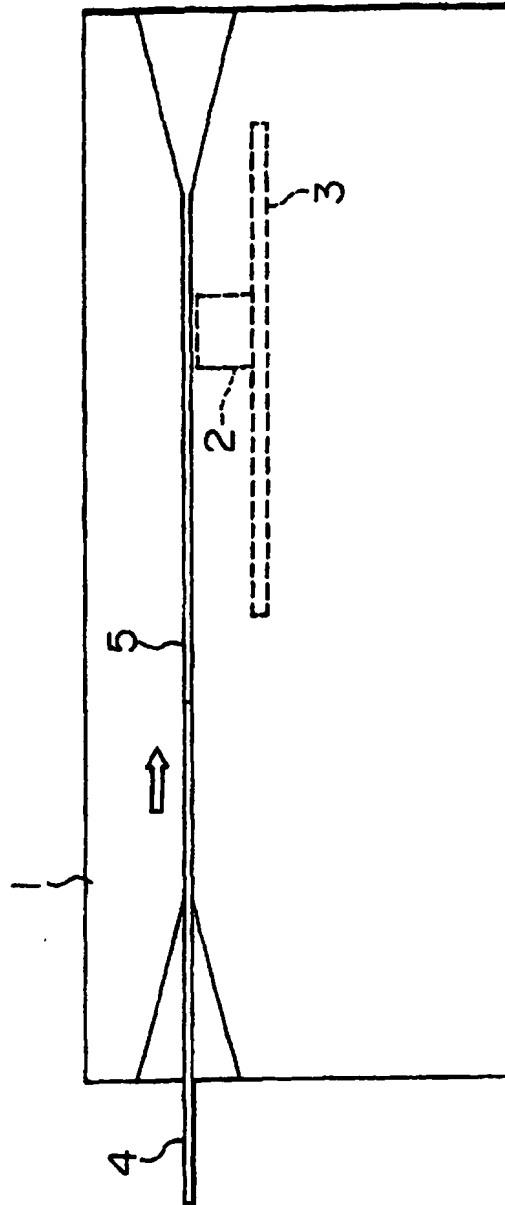


FIG. 2

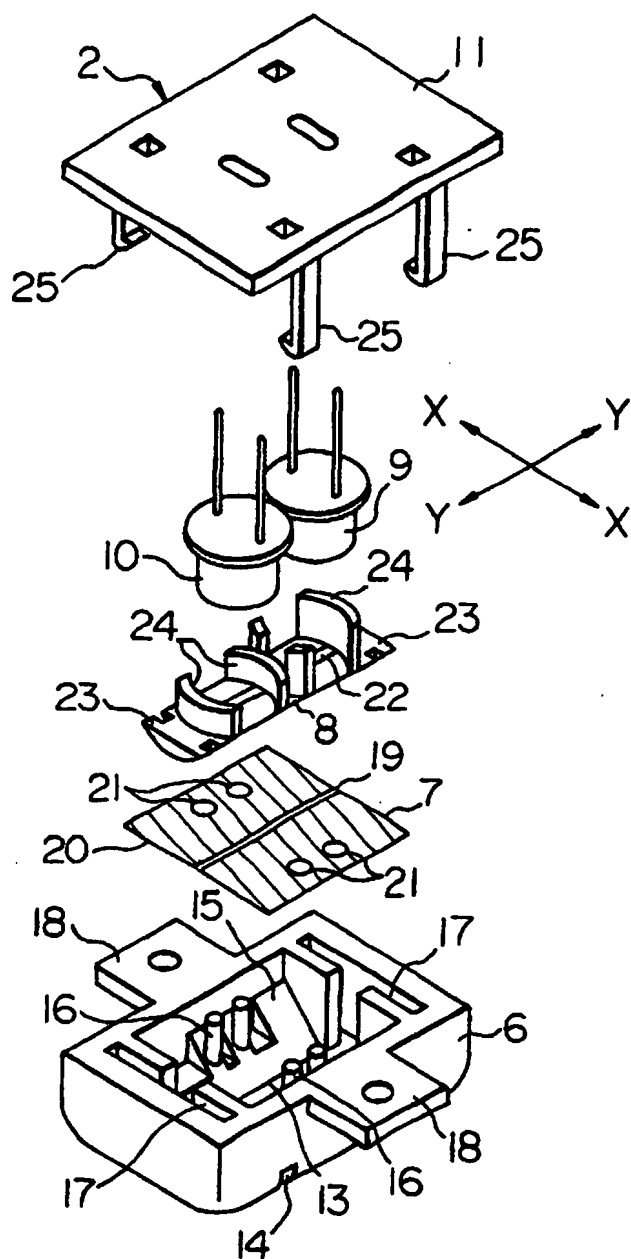


FIG. 3

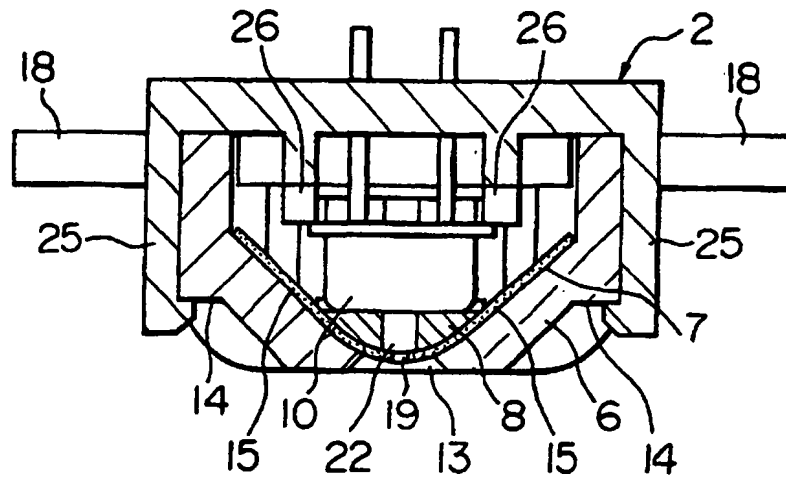


FIG. 4

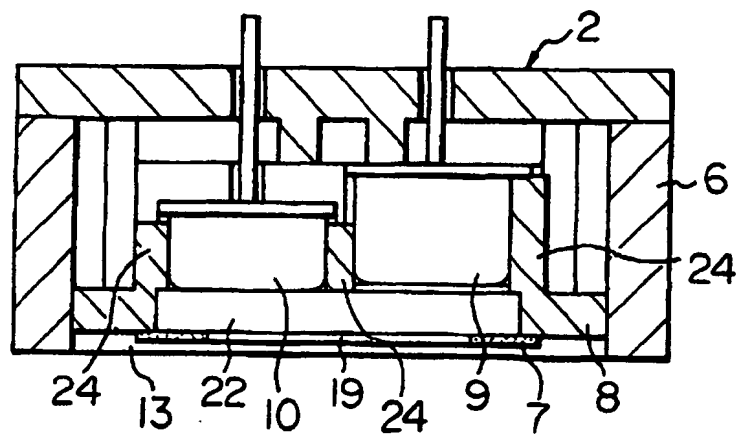


FIG. 5

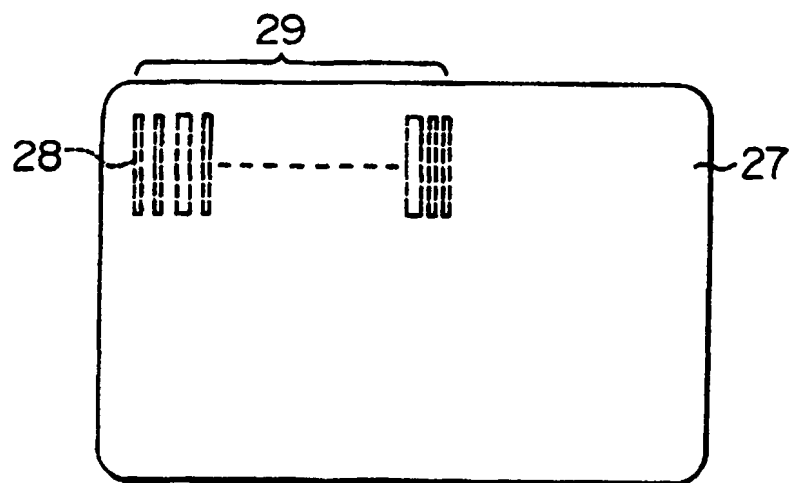


FIG. 6

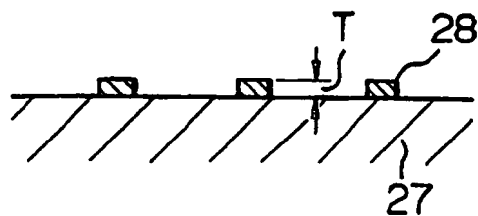
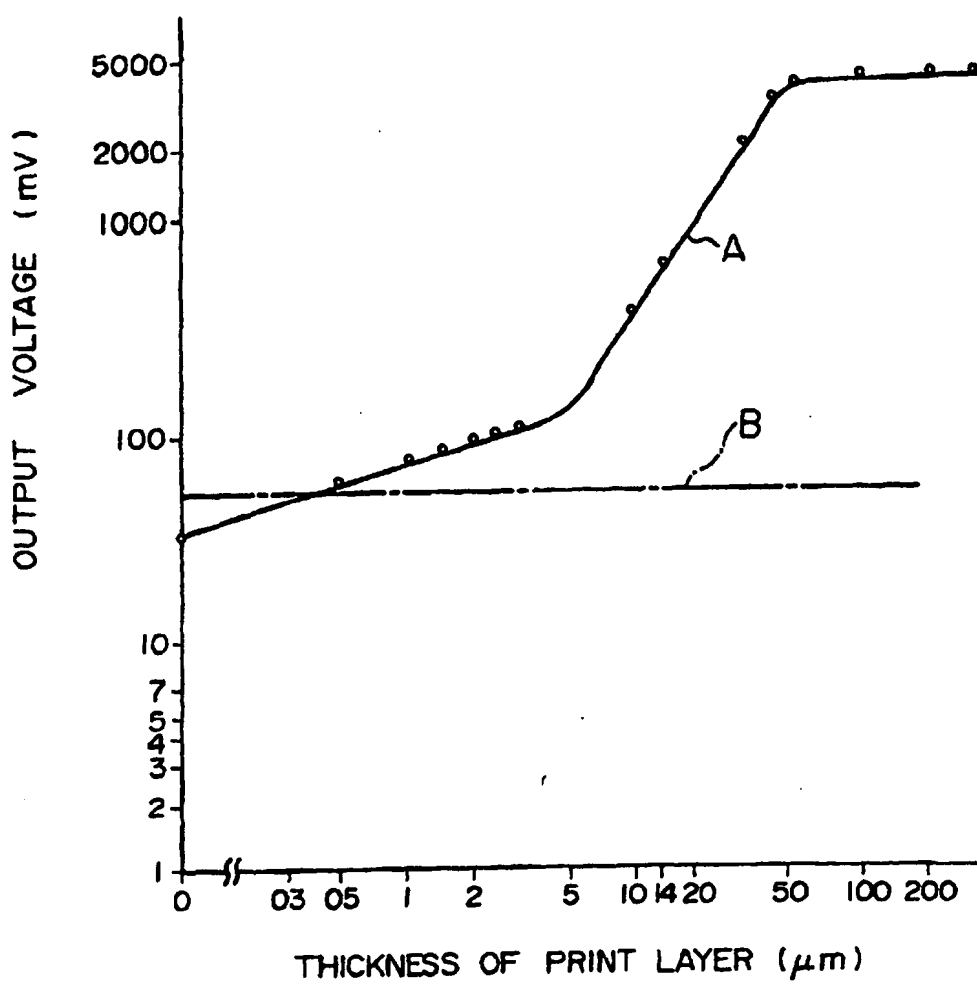


FIG. 7



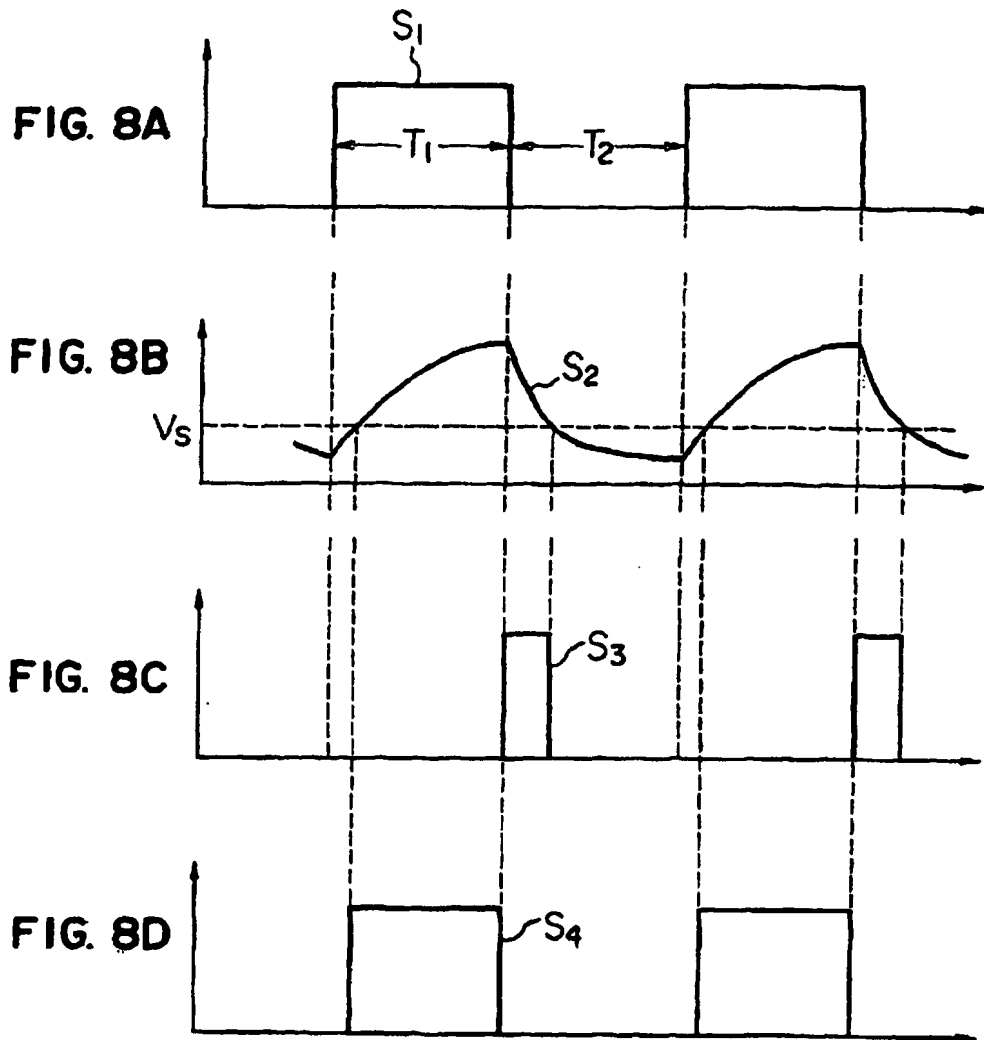


FIG. 9A EXAMPLE 1

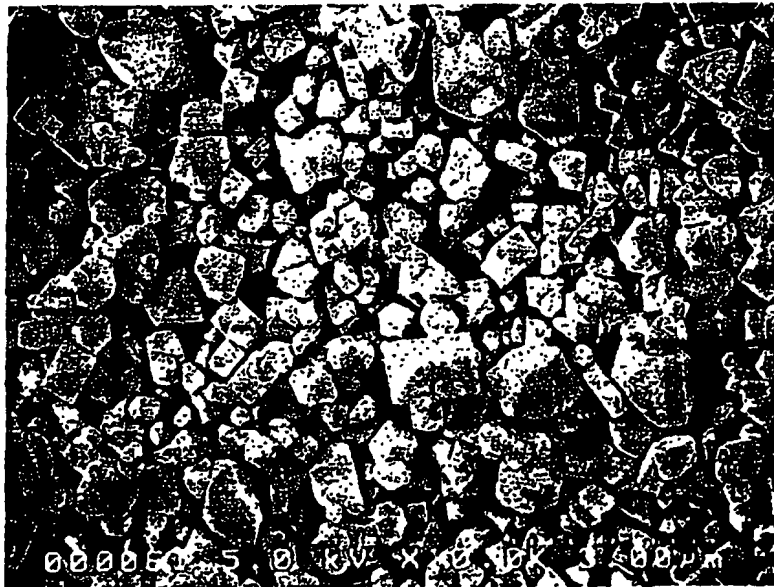


FIG. 9B COMPARATIVE EXAMPLE



FIG. 9C EXAMPLE 10

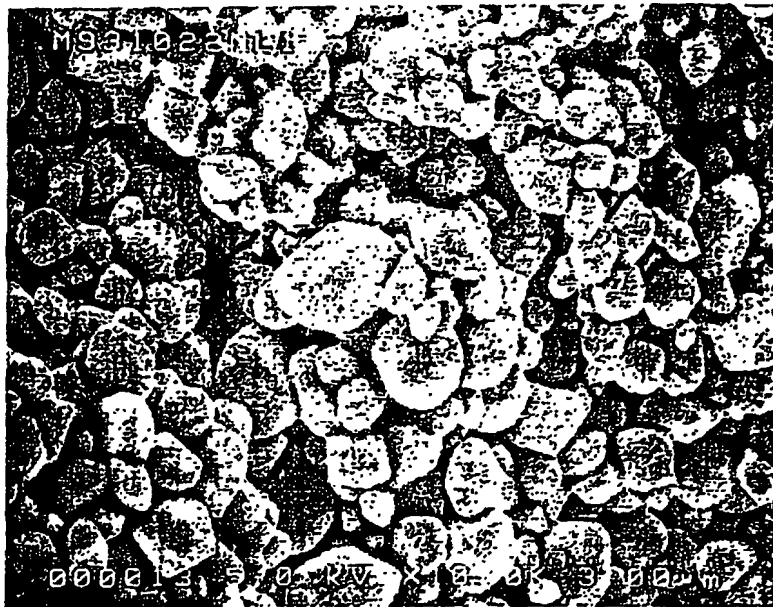


FIG. 10A

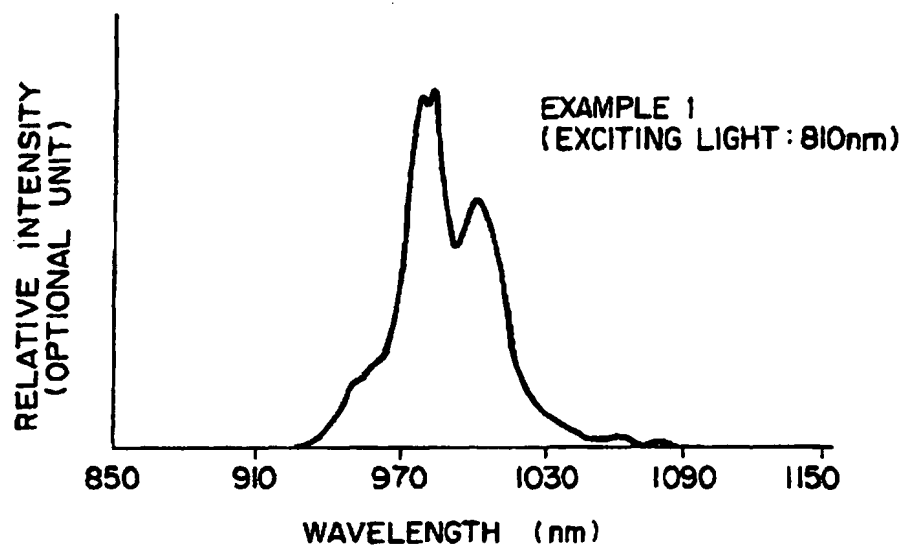


FIG. 10B

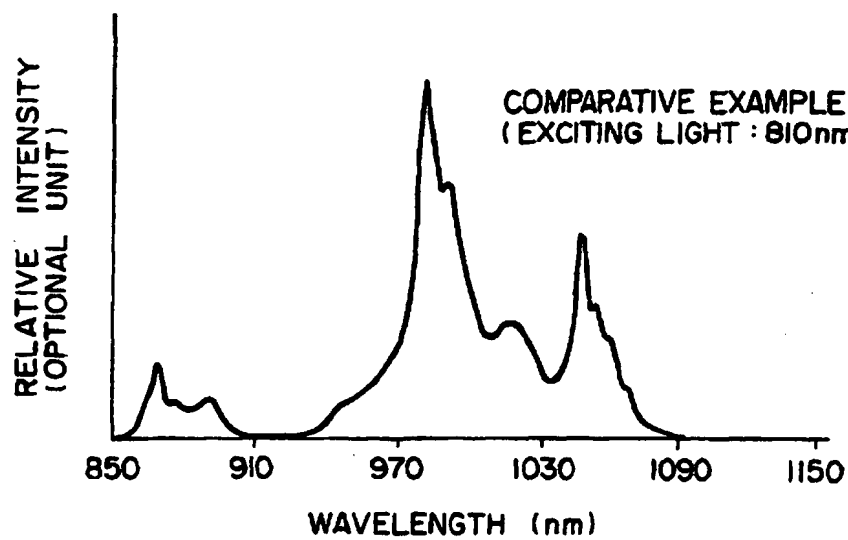


FIG. 11

